

These disadvantages have hindered the development of wet oxidation as a method for treating waste. Accordingly, it is an object of the present invention to provide a wet oxidation process which goes some way to overcoming these limitations, or at least provides the public with a useful choice.

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SUMMARY OF INVENTION

In a first aspect, the present invention provides a process for oxidising a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:

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- (a) subjecting said feedstock to temperature and pressure to produce a fluid phase and a vapour phase;
- (b) contacting the feedstock of (a) with an oxidant to produce a vapour phase comprising at least some oxidation products; and
- 15 (c) separating said vapour phase from said fluid phase.

The non-volatile oxidisable material may be a single substance or a mixture of substances, and may be a waste product such as industrial waste, consumer waste or a component thereof, all of which are well known in the art.

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Generally the oxidisable material comprises an organic substance.

Preferably, the oxidisable material comprises one or more components selected from the group consisting of: lipids; proteins; carbohydrates (for example starch or cellulose); mineral oils; vegetable oils; waxes; and hydrocarbons.

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Optionally, the oxidisable material includes one or more oxidisable inorganic compounds.

Oxidants which may be used in a process of the invention include, but are not limited to air, oxygen, ozone, peroxide, and mixtures thereof. Preferably, the oxidant is air, oxygen or peroxide.

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The temperature at which the process is operated is generally between about 100°C and about 350°C and the pressure between 0.7 and 17.2 MPa.

5 Preferably, the temperature at which the process is operated is between about 190°C and about 300°C, more preferably between about 190°C and about 280°C. In two particularly preferred embodiments, the temperature is between about 190°C and about 210°C or between about 220°C and about 240°C.

10 Preferably, the pressure at which the process is operated is between about 1.4 MPa and about 13.0 MPa, more preferably between about 2.0 MPa and about 3.5 MPa. In two particularly preferred embodiments, the pressure is between about 2.1 MPa and about 2.9 MPa or between about 2.9 MPa and about 3.4 MPa.

15 The process of the invention is particularly applicable to the treatment of industrial and consumer waste.

Optionally, a catalyst may be employed to increase the rate of reaction. Suitable catalysts include, but are not limited to, the transition metal ions and mixtures thereof. Preferably, the catalyst is copper (II) ions, iron (II) ions or manganese (II) ions, or a mixture thereof.
20 More preferably, the catalyst is copper (II) ions.

Desirably, oxidation is carried out as a continuous process wherein the feedstock is continuously introduced into the reactor and the vapour phase continuously removed from the reactor.

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The oxidation products in the separated vapour phase may be recovered by reducing the temperature and pressure of the vapour phase. Accordingly, in another aspect, the present invention provides an oxidation product when produced by a process of the invention.

30 In a preferred embodiment, the oxidation product is acetic acid, formic acid, carbon dioxide or a mixture thereof.

In another aspect, the present invention provides a non-volatile salt when produced by an oxidation process of the invention.

5 Although the present invention is broadly as defined above, those persons skilled in the art will appreciate that the invention is not limited thereto and that the invention also includes embodiments of which the following description gives examples.

DESCRIPTION OF THE DRAWINGS

10 Figure 1 is a schematic diagram of apparatus particularly suitable for performing an oxidation process of the invention on a laboratory scale.

Figure 2 is a schematic diagram of the additional modifications which may be made to the apparatus of Figure 1 to facilitate the treatment of slurries.

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Figure 3 is a schematic diagram of a proposed pilot plant or commercial plant design.

Figure 4 is a graph of COD and temperature vs time for the oxidation of glucose at 200°C in a process of the invention.

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Figure 5 is a graph of pH and temperature vs time for oxidation of glucose at 200°C in a process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

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The present invention is broadly directed to the oxidation of various substances, conveniently described herein as "Phase Transfer Wet Oxidation".

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Accordingly, in a first aspect, the present invention provides a process for oxidising a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:

- (a) subjecting said feedstock to temperature and pressure to produce a fluid phase and a vapour phase;
- (b) contacting the feedstock of (a) with an oxidant to produce a vapour phase comprising at least some oxidation products; and
- 5 (c) separating said vapour phase from said fluid phase.

The term "feedstock" as used herein includes, but is not limited to, aqueous liquids, solutions, suspensions, colloids, emulsions, and other mixtures. The term may also include slurries formed from substantially dry material to which is added a suitable
10 aqueous liquid.

The amount of oxidisable material in the feedstock is typically less than about 10% by weight.

- 15 In one embodiment, the feedstock is fed directly into the apparatus. In an alternative embodiment, water is firstly introduced into the apparatus and then the oxidisable material is introduced into the apparatus.

The term "contact" as used herein generally means admixing the aqueous solution or
20 slurry with the oxidant in a suitable apparatus, hereinafter referred to as the "reactor", which is of a type designed to withstand the temperature and pressure and is well known in the art. Suitable reactors include, but are not limited to autoclaves and pressure reactors.

- 25 The term "non-volatile" as used herein means that the oxidisable material is largely in the solid or liquid state under the temperature and pressure conditions in the reactor.

It will be appreciated that, preferably, the reactor is one in which the interfacial area between the oxidant and the feedstock is maximised, and from which the reaction
30 products and the volatile non-oxidisable components present in the feedstock (for example, water) may be readily removed in the vapour phase.

The term "separate" as used herein generally means removing the vapour phase from the reactor while excluding the fluid phase.

5 In one embodiment, phase separation may be achieved by keeping the reaction pressure near to the vapour pressure of water at the reaction temperature by, for example, rapidly lowering the pressure of the reactor to remove volumes of treated material by flash vaporisation at specific intervals.

10 The feedstock may be introduced into the reactor by means of a pump or hydraulic plunger or by other means as are known in the art. Optionally, the apparatus may incorporate a means of stirring the contents, if and when required.

15 It will be appreciated that the temperature and pressure at which the process of the invention is operated are selected according to the stability or ease of oxidation of the feedstock. The temperature at which the process is operated is generally between about 100°C and 350°C and the pressure between about 0.7 MPa and about 17.2 MPa.

20 Preferably, the temperature at which the process is operated is between about 190°C and about 300°C, more preferably between about 190°C and about 280°C. In two particularly preferred embodiments, the temperature is between about 190°C and about 210°C or between about 220°C and about 240°C.

25 Preferably, the pressure at which the process is operated is between about 1.4 MPa and about 13.0 MPa, more preferably between about 2.0 MPa and about 3.5 MPa. In two particularly preferred embodiments, the pressure is between about 2.1 MPa and about 2.9 MPa or between about 2.9 MPa and about 3.4 MPa.

30 The present invention also contemplates processes in which the feedstock is at the desired temperature and/or pressure prior to entering the reactor, for example a process in which the feedstock comprises a mixture of non-volatile oxidisable material and superheated steam.

While the oxidisable substances are relatively non-volatile, their primary wet oxidation products are generally much more volatile compounds such as carbon dioxide, acetic acid, and formic acid. It will therefore be understood that while the feedstock is introduced to the reactor in the liquid or solid phase, the products of the oxidation reaction may be removed from the reactor in the vapour phase, hence the name "Phase Transfer Wet Oxidation".

Accordingly, a significant portion of the oxidation products from a process of the invention is removed in the gas phase. This is in contrast to the known processes in which the reaction products are generally removed in the liquid phase.

It will be appreciated that any compound which is volatile at the reaction temperature may be present in the gas phase. However, any higher molecular weight compounds, such as higher organic acids, will generally be present at very low concentrations.

The oxidation products in the separated vapour phase may be recovered by reducing the temperature and pressure of the vapour phase. Accordingly, in another aspect, the present invention provides an oxidation product when produced by an oxidation process of the invention.

Typical oxidation products include, but are not limited to, carbon dioxide, formic acid, acetic acid, higher organic acids and mixtures thereof.

In a preferred embodiment, the oxidation product is acetic acid, formic acid, carbon dioxide or a mixture thereof.

More preferably, the oxidation product is acetic acid or a mixture of acetic acid and formic acid. The acetic acid so provided is sterile. Accordingly, the acetic acid may be converted to acetate and utilised as a nutrient source for micro-organisms.

Advantageously, the temperature and pressure of the vapour phase is reduced in a heat exchanger and the heat recycled to the incoming feedstock. In another embodiment, the

incoming feedstock and the reactor contents are optionally heated by the addition of external heat.

Desirably, oxidation may be carried out as a continuous process wherein the feedstock is continuously introduced into the reactor and the vapour phase continuously removed.

When the oxidation is carried out as a continuous process the reactor will advantageously incorporate a means of measuring the fluid level within the reactor, such that the reactor does not run dry.

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If a mixture of oxidisable substances is subjected to a process of the invention, then those with a faster rate of reaction will oxidise first, and the products of the reaction are removed in the vapour phase as they are formed. More stable substances, with a correspondingly slower rate of reaction, will remain in the reactor until they have oxidised to volatile products. Any water in the feedstock entering the reactor will also be vaporised, thereby permitting more feedstock to enter the reactor. This is in contrast to the known processes, which require either a large reactor, or provide a reduction in the percent conversion of oxidisable substances to their oxidation products.

Optionally, a catalyst may be employed to increase the rate of reaction. Suitable catalysts include, but are not limited to, the transition metal ions and mixtures thereof. Preferably, the catalyst is copper (II) ions, iron (II) ions or manganese (II) ions, or a mixture thereof. More preferably, the catalyst is copper (II) ions.

While it will be appreciated that the process of the invention is amenable to heterogeneous catalysis, the catalyst may advantageously be in the form of a homogenous catalyst. In the known processes, the use of homogenous catalysts generally leads to catalyst leaching and subsequent contamination of the downstream products. However, it will be appreciated that, in a process of the present invention, the catalyst may remain in the dissolved liquid phase in the reactor. In this way an initial amount of catalyst may be introduced into the reactor, where it will remain while multiple volumes of feedstock are introduced into the reactor and the oxidation products removed in the vapour phase.

exchanger HX2 which may recycle the heat recovered from the oxidation products removed in the vapour phase by cool-down heat exchanger HX3. It will be appreciated that the feedstock need be heated only to make up the heat balance of the reaction.

- 5 An oxidant would be introduced into the reactor vessel through inlet GI1. Contact between the oxidant and the fluid phase will then be promoted by means of a stirrer STR2 which mixes the reactor contents. The fluid level within the reactor may be monitored by a system of level sensors LS1 connected to a suitable process control system.
- 10 The temperature of the fluid phase in the reactor would be controlled by a heating unit and heat exchanger HX4 by means of the recirculating loop RL1 and pump LP4. HX4 may also recycle the heat recovered from the oxidation products removed in the vapour phase by cool-down heat exchanger HX3
- 15 The vapour phase products of the oxidation reaction would be separated from the fluid phase and removed from the reactor through cool-down heat exchanger HX3. The temperature and pressure of the product stream is thereby reduced. The resultant product stream would pass into liquid trap LT2 where gas phase reaction products such as carbon dioxide may be recovered from the mix of uncondensed gases at outlet GO1 while liquid
- 20 phase reaction products such as water, formic acid and acetic acid may be recovered at outlet LO1.

- The reactor could be emptied, when required, through outlet LO2 and the heat from the reactor contents may be recovered by heat exchanger HX5. Accordingly, useful non-
- 25 volatile salts which accumulate in the reactor may be recovered and any catalyst used may be recycled or subject to suitable disposal.

INDUSTRIAL APPLICATION

- 30 It will be appreciated that, in use, the present invention provides a process for oxidising a feedstock which may be applied to the treatment of industrial waste. Advantageously, the reactor may be of a significantly smaller volume than that used in known processes due to the removal of both water and volatile oxidation products from the reactor in the vapour

phase, allowing for further feedstock to enter the system. In this way the process may be operated in a continuous manner.

5 In addition, a homogenous catalyst may be used in the treatment of more stable compounds, and the catalyst retained in the reactor while multiple volumes of waste were treated. A variety of consumer and industrial waste is amenable to treatment by a process of the invention, and these are discussed above.

10 Furthermore, the present invention also provides a sterile source of, for example, acetic acid which may be utilised, following conversion to acetate, as a nutrient source for micro-organisms.

15 Those persons skilled in the art will further appreciate that the present description is provided by way of example only and that the scope of the invention is not limited thereto.

REFERENCES

- 20 1. Kolackowski, S., Plucinski, P., Beltran, F., Rivas, F., McLurgh, D. "Wet air oxidation: a review of process technologies and aspects in reactor design", *Chem. Eng. J. (Lausanne)*, 1999, 73, 2, 143-160.

CLAIMS

1. A process for oxidising a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:
 - 5 (a) subjecting said feedstock to temperature and pressure to produce a fluid phase and a vapour phase;
 - (b) contacting the feedstock of (a) with an oxidant to produce a vapour phase comprising at least some oxidation products; and
 - (c) separating said vapour phase from said fluid phase.
- 10 2. A process as claimed in claim 1 wherein the feedstock is an aqueous liquid, solution, suspension, colloid, emulsion or other mixture.
- 15 3. A process as claimed in claim 1 or 2 wherein the feedstock comprises a slurry formed from substantially dry material to which is added an aqueous liquid.
4. A process as claimed in any one of claims 1 to 3 wherein the oxidisable material comprises less than about 10% by weight of the feedstock.
- 20 5. A process as claimed in any one of claims 1 to 4 wherein the oxidisable material comprises a mixture of substances.
6. A process as claimed in any one of claims 1 to 5 wherein the oxidisable material is a waste product.
- 25 7. A process as claimed in claim 6 wherein the waste product is industrial waste, consumer waste or a component thereof.
- 30 8. A process as claimed in claim 6 or claim 7 wherein the oxidisable material is waste selected from the group consisting of: dairy shed waste; pig and chicken waste; milk processing plant waste; milk, cheese and butter vat wash downs; food processing waste; waste from the wine industry and brewing industry; food waste; shipboard waste; waste in environmentally sensitive locations; waste from the

wash downs and oil-traps of petroleum service stations and garages; waste fats and proteins from the meat processing industry; wool-scouring waste; sewage; medical waste; fibre, ink and polymeric material from the deinking waste produced in the recycling of paper; waste paper and paper products; waste from the wood processing industry including waste wood and wood products, wood fibre, saw dust and wood treated with preservatives; rubber waste; plastic waste; and tannin and colorants from wood pulping streams.

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9. A process as claimed in any one of claims 1 to 8 wherein the process is applied to the reclamation of sites contaminated by organic materials.

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10. A process as claimed in claim 9 wherein said site is selected from the group consisting of: petrochemical works; gas works; timber treatment sites; and agrochemical sites.

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11. A process as claimed in any one of claims 1 to 7 wherein the oxidisable material comprises an organic substance.

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12. A process as claimed in claim 11 wherein the organic substance is selected from the group consisting of: lipids; proteins; carbohydrates; mineral oils; vegetable oils; waxes; and hydrocarbons.

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13. A process as claimed in claim 12 wherein the organic substance is a carbohydrate selected from starch and cellulose.

14. A process as claimed in any one of claims 1 to 13 wherein the oxidisable material includes one or more oxidisable inorganic compounds.

15. A process as claimed in any one of claims 1 to 14 wherein the oxidant is selected from the group consisting of: air; oxygen; ozone; peroxide; and mixtures thereof.

16. A process as claimed in claim 15 wherein the oxidant is selected from the group consisting of: air; oxygen; and peroxide.

17. A process as claimed in any one of claims 1 to 16 wherein the temperature is between about 100°C and about 350°C.
18. A process as claimed in any one of claims 1 to 17 wherein the temperature is
5 between about 190°C and about 300°C.
19. A process as claimed in any one of claims 1 to 18 wherein the temperature is between about 190°C and about 280°C.
- 10 20. A process as claimed in any one of claims 1 to 19 wherein the temperature is between about 190°C and about 210°C.
21. A process as claimed in any one of claims 1 to 19 wherein the temperature is between about 220°C and about 240°C.
- 15 22. A process as claimed in any one of claims 1 to 20 wherein the pressure is between about 0.7 MPa and about 17.2 MPa.
23. A process as claimed in any one of claims 1 to 22 wherein the pressure is between
20 about 1.4 MPa and about 13.0 MPa.
24. A process as claimed in any one of claims 1 to 23 wherein the pressure is between about 2.0 MPa and about 3.5 MPa.
- 25 25. A process as claimed in any one of claims 1 to 24 wherein the pressure is between about 2.1 MPa and about 2.9 MPa.
26. A process as claimed in any one of claims 1 to 24 wherein the pressure is between about 2.9 MPa and about 3.4 MPa.
- 30 27. A process as claimed in any one of claims 1 to 25 wherein the feedstock of (a) is contacted with the oxidant in the presence of a catalyst.

28. A process as claimed in claim 27 wherein the catalyst is a homogenous catalyst.
29. A process as claimed in claim 27 or claim 28 wherein the catalyst is selected from the group consisting of the transition metal ions and mixtures thereof.
- 5 30. A process as claimed in any one of claims 27 to 29 wherein the catalyst is selected from the group consisting of: copper (II) ions; iron (II) ions; manganese (II) ions; and mixtures thereof.
- 10 31. A process as claimed in any one of claims 27 to 30 wherein the catalyst is copper (II) ions.
32. A process as claimed in any one of claims 1 to 31 wherein oxidation is carried out as a continuous process wherein the feedstock is continuously introduced into a reactor and the vapour phase continuously removed from the reactor.
- 15 33. A process as claimed in any one of claims 1 to 32 wherein the vapour phase is separated from the fluid phase by flash vaporisation.
- 20 34. A process as claimed in any one of claims 1 to 33 further including the step of reducing the temperature and pressure of the vapour phase to recover at least one oxidation product.
- 25 35. A process as claimed in claim 34 wherein the oxidation product is selected from the group consisting of: carbon dioxide; formic acid; acetic acid; higher organic acids; and mixtures thereof.
- 30 36. A process as claimed in claim 34 or claim 35 wherein the oxidation product is selected from the group consisting of: acetic acid; formic acid; carbon dioxide and mixtures thereof.
37. An oxidation product when produced by a process as claimed in any one of claims 34 to 36.

38. A process as claimed in any one of claims 1 to 36 further comprising the step of recovering at least one non-volatile salt from the fluid phase.
39. A process as claimed in claim 38 wherein the non-volatile salt is recovered as a concentrated solution or a precipitate.
40. A process as claimed in claim 38 or claim 39 wherein the non-volatile salt is an inorganic wood preservative.
41. A non-volatile salt when produced by a process as claimed in any one of claims 38 to 40.